**Detailed Discussion on Application of Kinetic Model to Chemisorption Rates**

**2.2 Kinetic Model for Chemisorption.**

To obtain a quantitative picture of the chemisorption rate we use kinetic theory to derive an expression for the number of molecules in the gas phase and then obtain effective chemisorption barriers by fitting the resulting kinetic expression to our data. We derive the appropriate rate expression for chemisorption as follows:

The change in the number of molecules ( $N$ ) in the gas phase can be written in terms of the rates of adsorption ( $R_a$ ) and desorption ( $R_d$ ) from the particle surface:

$$\frac{dN}{dt} = -NR_a + (N_s)R_d \qquad \textbf{(1)}$$

where $N_s$ is the number of molecules chemisorbed to the surface. If the rate of desorption is negligible we can ignore the second term so that:

$$\frac{dN}{dt} = -NR_a \quad \textbf{(2)}$$

We expect the rate of chemisorption be proportional to the product of the collision rate with the surface (which is proportional to the average molecular velocity, $\bar{v}$, and hence to the square root of the temperature, $\sqrt{\mathrm{T}}$), the probability of having enough energy to overcome the reaction barrier (which is proportional to the Boltzmann factor, $e^{-\frac{E_a}{k_B \mathrm{T}}}$), and the fraction of the surface sites which are unoccupied, and hence available for reaction (which is proportional to $M - N_s$, where $M$ is the total number of surface sites occupied at monolayer coverage and $N_s$ is the number of molecules already adsorbed to the surface). Writing $\mathrm{M} = M - N_0$, where $N_0$ is the initial number of gas phase molecules, the rate equation becomes:

$$\frac{dN}{dt} = -N(\mathrm{M}+N)\Lambda\sqrt{\mathrm{T}}e^{\frac{-E_a}{k_B\mathrm{T}}} \quad \textbf{(3)}$$

where the constant $\Lambda$ includes all other factors. Assuming a constant rate of temperature increase and changing variables to $\tau = \frac{E_a}{k_B\mathrm{T}}$, separates the variables, leading to:

$$\frac{dN}{N(N+\mathrm{M})} = -A\tau^{-\frac{5}{2}}e^{-\tau}d\tau \quad \textbf{(4)}$$

where the pre-exponential factor is $A = \Lambda\left(\frac{dt}{d\mathrm{T}}\right)\left(\frac{1}{k_B^3 E_a^5}\right)^{\frac{1}{2}}$. Integrating both sides leads to:

$$\ln\left(\frac{N(\mathrm{M}+N_0)}{N_0(\mathrm{M}+N)}\right) = -\frac{3A\mathrm{M}}{4}\left\{\sqrt{\pi}erf\left(\sqrt{\frac{E_a}{k_B\mathrm{T}_0}},\sqrt{\frac{E_a}{k_B\mathrm{T}}}\right) + e^{-\frac{E_a}{k_B\mathrm{T}}}\sqrt{\frac{k_B\mathrm{T}}{E_a}}\left(1-\frac{2k_B\mathrm{T}_0}{E_a}\right) - e^{-\frac{E_a}{k_B\mathrm{T}_0}}\sqrt{\frac{k_B\mathrm{T}_0}{E_a}}\left(1-\frac{2k_B\mathrm{T}_0}{E_a}\right)\right\} \quad \textbf{(5)}$$

where $N$ is the instantaneous number of gas phase molecules and T is the instantaneous temperature $\mathrm{T}$, ( $\mathrm{T}_0$ = 500 K is the initial T).

We estimate $\mathrm{M}$ as follows: The catalyst particle is approximately spherical with a radius of 11Å, leading to a surface area of 1521Å$^2$. An alternate estimate of the surface area is the solvent accessible surface, which is 1750 Å$^2$ (using a probe radius of 4.0 Å). We assume that the particle surface is similar to the Ni(111) surface, which leads to 5.41Å$^2$ per three-fold site, indicating that the cluster has about 280 three-fold surface sites. As described in the various sections, this information is used to estimate $\mathrm{M}$ for each hydrocarbon species investigated. The $N$ as a function of time from RD simulations is used to calculate the left hand side of **(5)**. Then the $A$ and $E_a$ parameters are fit to the right hand side to the data (least squares fit using the solver in Microsoft Excel [17]).

To analyze quantitatively the chemisorption rates from our RD simulations, we utilize the kinetic model derived in section **2.2**, where to make the problem tractable we

assumed a negligible rate of desorption from the surface. This seems appropriate for ethyne, however, the concentration of gas phase ethene begins to show signs of desorption (e.g. near 1500 K). Propene and benzene show even stronger signs of desorption events, making it less likely that they would be well described by our model. Thus we will apply our kinetic model to methane, cyclohexane and ethyne chemisorption and then use other means to compare ethene, propene and benzene with them.

### 3.4.1 Methane (Figure 11a)

To apply our kinetic model to methane chemisorption we need to estimate M. To do this we assume that either H or $CH_3$ occupies alternate three-fold site, (leaving half the three-fold sites empty) leading to $M = 70$. Since $N_0 = 120$ methane molecules, we use $\mathrm{M} = M - N_0 = -50$.

Using values of N from our RD simulation we plot the LHS of **(5)** in **Figure 11a** and fit the RHS of **(5)** to these values by optimizing the $A$ and $E_a$ parameters**.** This leads to an apparent activation energy for chemisorption of $E_a$ = 41 kcal/mol. This is incompatible with the calculated activation energies on Ni(111), where ReaxFF leads to 18.4 kcal/mol [14], in good agreement the experimental value of 17.7 kcal/mol [2] and the QM activation energy of 18.9 kcal/mol. [19] This seems to invalidate the simplifying assumptions in our kinetic model, because an even lower barrier would be anticipated for chemisorption on such a defect rich surface. Indeed, steps are expected to lower the activation energy for both chemisorption and dehydrogenation [53, 54]. Thus, we expect that a typical barrier for chemisorption of a $CH_4$ onto our nanoparticle would be less than 15 kcal/mol, rather than higher than 40 kcal/mol.

### 3.4.2 Cyclohexane (Figure 11b)

The application of our kinetic model to cyclohexane chemisorption yields similar results. Assuming that each chemisorbed molecule in a complete monolayer on Ni(111) occupies eight three-fold sites results in an activation energy of $E_a$ = 31.3 kcal/mol. This is also much higher than expected.

### 3.4.3 Ethyne (Figure 11c)

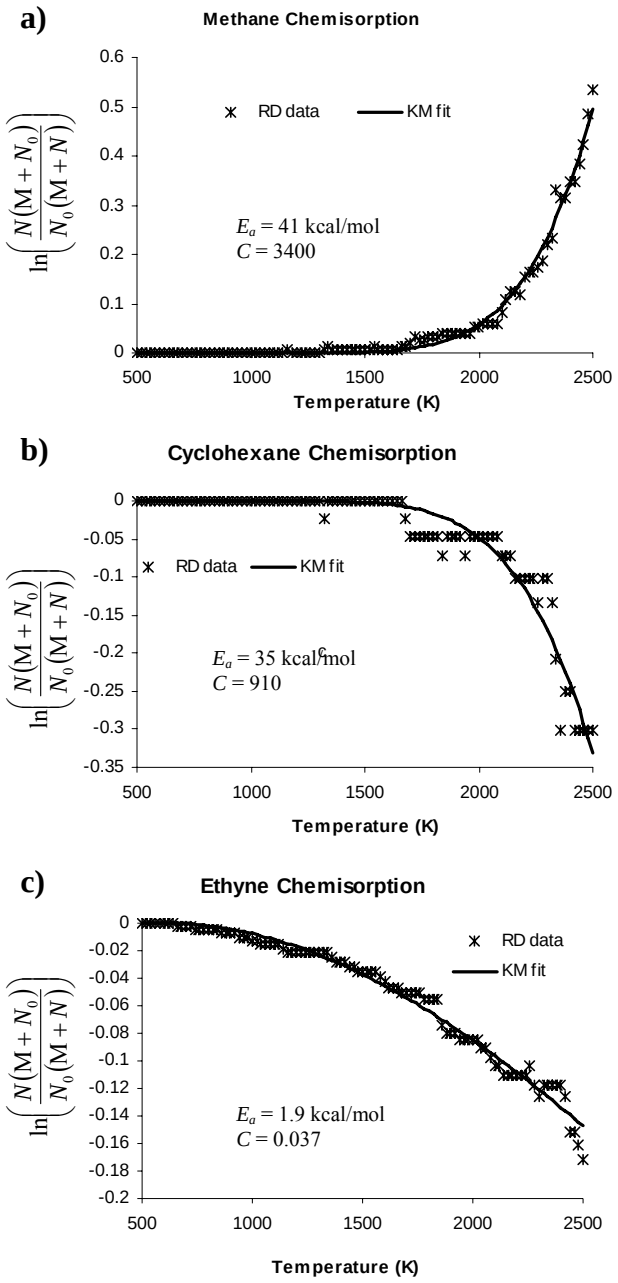
In contrast to the cases of methane and cyclohexane, breaking a C-H bond is not required for ethyne to chemisorb onto the nickel particle. Instead the C sp orbitals rehybridize with p orbitals from one of the π bonds to form $sp^2$ orbital on each C that can form σ bonds to the surface. Assuming each ethyne molecule in a complete monolayer on Ni(111) occupies 4 three-fold sites, our kinetic model leads to an activation energy of 1.9 kcal/mol (**Figure 11c**). Because ethyne binds strongly to Ni(111) (57 kcal/mol), and has electron density in a π bond readily able to do so, we expect a negligible barrier for chemisorption. This is consistent with the analysis of a kinetic model, with the nearly constant adsorption rate observed in our RD.

### 3.4.4 Ethene, Propene, and Benzene (Figure 12)

Like ethyne, we expect ethene, propene and benzene to have small chemisorption barriers. However, because they bind more weakly to the particle surface, we observe a significant number of desorption events as the temperature increases, making application of our simple chemisorption kinetic model inappropriate. Nevertheless we can gain insight into these chemisorption processes by comparing their relative rates during the first 25 ps of RD before desorption is observed.

Assuming that chemisorption barriers are negligible, the rate of chemisorption is equal to the rate of collision times the sticking co-efficient. The collision frequency per

molecule should be the same for each species except for the $1/\sqrt{m}$ factor from the Boltzmann velocity distribution. Thus **Figure 12** compares the relative sticking coefficients of each species. Ethyne and ethene have similar molecule weights and sticking coefficients (examining the entire duration of the dynamics suggests that the rate of ethyne chemisorption is twice the rate of ethene adsorption as noted earlier). Despite propene's higher molecule weight it has a higher chemisorption rate than either ethyne or ethene, showing that it has a higher sticking coefficient, which is even higher for benzene. This is expected from the larger number of low frequency modes that can absorb some of the collision energy to better trap the molecule on the surface.




**d)** KM fit—equation **(5)**:

$$\ln\left(\frac{N(M+N_0)}{N_0(M+N)}\right) = C\left\{\sqrt{\pi}erf\left(\sqrt{\frac{E_a}{k_BT_0}},\sqrt{\frac{E_a}{k_BT}}\right)+e^{-\frac{E_a}{k_BT}}\sqrt{\frac{k_BT}{E_a}}\left(1-\frac{2k_BT_0}{E_a}\right)-e^{-\frac{E_a}{k_BT_0}}\sqrt{\frac{k_BT_0}{E_a}}\left(1-\frac{2k_BT_0}{E_a}\right)\right\}$$

**Figure 11:** The kinetics of chemisorption of **a)** methane, **b)** cyclohexane, and **c)** ethyne on the $Ni_{468}$ nanoparticle from ReaxFF RD compared to the rate expression from **d)** kinetic model (KM) for chemisorption—equation **(5)**.

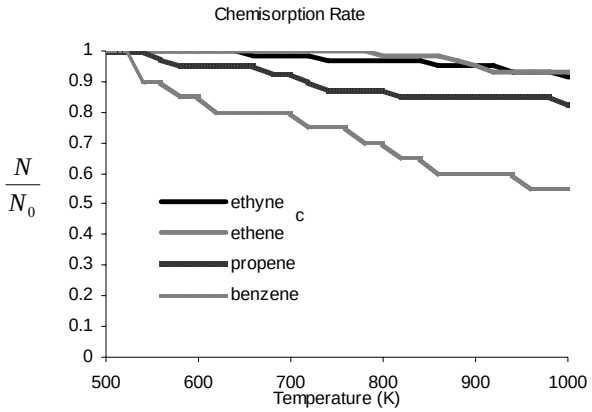



**Figure 12:** Relative **r**ates of chemisorption for unsaturated hydrocarbons during first 25 ps of RD, before desorption is noticeable.